

Very Unusual Magnetic Properties in Multi-walled Carbon Nanotube Mats

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We report magnetic measurements up to 1100 K on a multi-walled carbon nanotube mat sample using a Quantum Design vibrating sample magnetometer. In an ultra-low field ($H = -0.02$ Oe), we find a very large paramagnetic susceptibility (up to 12.7% of $1/4\pi$) at 1100 K and a very large diamagnetic susceptibility (at least 8.4% of $-1/4\pi$) at 482 K. A small magnetic field (2.1 Oe) completely suppresses the diamagnetic susceptibility at 482 K and reduces the paramagnetic susceptibility at 1100 K by a factor of over 20. We rule out explanations based on magnetic contaminants, instrument artifacts, and orbital diamagnetism. The magnetic data are inconsistent with any known physical phenomena except for granular superconductivity. The present results suggest the existence of an unknown new physical phenomenon or superconductivity with an ultra-high transition temperature.

The low-energy physics of an individual metallic single-walled carbon nanotube is shown to be equivalent to a two-leg Hubbard ladder [1], which can be described by a Luttinger liquid with an effective interaction parameter $K_{\rho+}$ (Refs. [2, 3]). Single-walled nanotube (SWNT) bundles and individual multi-walled nanotubes (MWNTs) are then equivalent to quasi-one-dimensional (quasi-1D) arrays of two-leg Hubbard ladders, which should be ideal candidates for high-temperature superconductivity [2, 3] especially if $K_{\rho+} \geq 1.5$ (Ref. [3]). The $K_{\rho+}$ value of a two-leg ladder can be determined from the temperature dependence of the resistance R , which follows $R \propto T^{2K_{\rho+}-2}$ (Ref. [3]). The on-tube resistance is found [4] to follow $R_{tube} \propto T^{1.72}$ for a SWNT with a diameter $d = 1.5$ nm (corresponding to $K_{\rho+} = 1.86$) and $R_{tube} \propto T^{1.48}$ for another SWNT with $d = 1.7$ nm (corresponding to $K_{\rho+} = 1.74$). The large $K_{\rho+}$ values imply that the long-range repulsive Coulomb interaction in these samples is effectively screened out so that strong electron-phonon interactions with the radial breathing mode [5] and other phonon modes may lead to a large effective attractive interaction. Therefore, SWNT bundles and MWNTs are ideal candidates for high-temperature superconductivity.

Very recently, quasi-1D superconductivity at about 12 K has been reported [6] in a short MWNT array where the normal-state resistance $R_N \propto T^{-0.8}$. Such a temperature dependence of R_N might suggest that $K_{\rho+} \leq 0.6$, leading to d -wave superconductivity [3]. Since any small disorder can suppress superconductivity dramatically in the case of $K_{\rho+} < 1$ (Ref. [3]), the intrinsic superconducting transition temperature in disorder-free MWNT arrays should be much higher. On the other hand, the resistance data [7] of an individual MWNT can be quantitatively explained in terms of quasi-1D superconductivity with a mean-field transition temperature $T_{c0} \simeq 260$ K [4, 8]. The normal-state on-tube resistance of this individual MWNT appears to follow a linear- T dependence [4, 7, 8], suggesting that $K_{\rho+} \simeq 1.5$. The larger $K_{\rho+}$ (> 1) and T_{c0} values found for this MWNT indicate that the long-range repulsive Coulomb interaction is more effectively screened out and/or the doping is more optimal.

Here we report magnetic measurements up to 1100 K on a MWNT mat sample using a Quantum Design vibrating sample magnetometer (VSM). In an ultra-low field ($H = -0.02$ Oe), we find a very large paramagnetic susceptibility (up to 12.7% of $1/4\pi$) at 1100 K and a very large diamagnetic susceptibility (at least 8.4% of $-1/4\pi$) at 482 K. A small magnetic field (2.1 Oe) completely suppresses the diamagnetic susceptibility at 482 K and reduces the paramagnetic susceptibility at 1100 K by a factor of over 20. The results are inconsistent with any known physical phenomena except for granular superconductivity with $T_{c0} > 1100$ K.

A purified MWNT mat sample is obtained from SES Research of Houston. The sample was prepared by chemical vapor deposition (CVD) using an iron catalyst. By burning off carbon related materials in air (thermal gravimetric analysis), we find the weight of the residual to be 1.0%. We determine the relative metal contents of the residual using a Perkin-Elmer Elan-DRCe inductively coupled plasma mass spectrometer (ICP-MS). From the ICP-MS result and the percentage of the residual, we obtain the metal-based impurity concentrations (ppm in weight): Na = 1210.3, Mg = 80.156, Al = 1645.5, Si = 184.43, K = 233.51, Ca = 1129.9, Sc = 2.027, Ti = 5.4618, V = 1.7611, Cr = 33.634, Mn = 10.953, Fe = 5225.1, Co = 2.7628, Ni = 10.354, and Cu = 224.24. The main magnetic impurities are Fe_2O_3 , as indicated by the energy dispersive x-ray (EDX) analysis. The Co concentration in this sample is less than 3 ppm, which is negligibly small.

Extensive magnetic measurements by both us and the staff of Quantum Design (up to 1100 K) on a control sample of Er_2O_3 show that—after correcting for an off-set moment of $(4.4\text{--}5.6) \times 10^{-7}$ emu due to the interaction between the VSM drive head and the pick-up coils—the absolute accuracy of the measurement is better than 1.0×10^{-7} emu at low fields (0.06–4.21 Oe) [9]. The data shown below are corrected for temperature-dependent offset moment: $(5.5 \times 10^{-7} - 4.4 \times 10^{-11}T)$ emu, which is determined from magnetic measurements on the control sample of Er_2O_3 cooled from $T = 1100$ K to 300 K

in a field of -0.018 Oe. The data are smoothed using cubic spline interpolation with a smoothing parameter $\Lambda = 4$. The stable low fields are obtained after the ultra low-field process leaves a slightly negative field at the sample position. Then the field is biased using a secondary coil wound on the vacuum sleeve and driven with a dc current. The field profile is obtained with the high-resolution flux gate whose absolute magnitude is verified with the paramagnetic standard sample.

Figure 1 shows the temperature dependence of the initial warm-up and cool-down susceptibilities in a field of -0.02 Oe for a 12.3 mg MWNT mat sample. The virgin sample was inserted into the sample chamber with the field of -0.02 Oe without going through the linear motor used for vibrating the sample. The maximum field the sample has experienced is the earth-field (about -0.5 Oe) before it experiences the field of -0.02 Oe. Therefore, any remanent magnetization due to superconductivity and/or magnetic impurities should be negative when the field is reduced from -0.5 Oe to -0.02 Oe. This will lead to an underestimate of the magnitude of the diamagnetic susceptibility because of the negative field (-0.02 Oe).

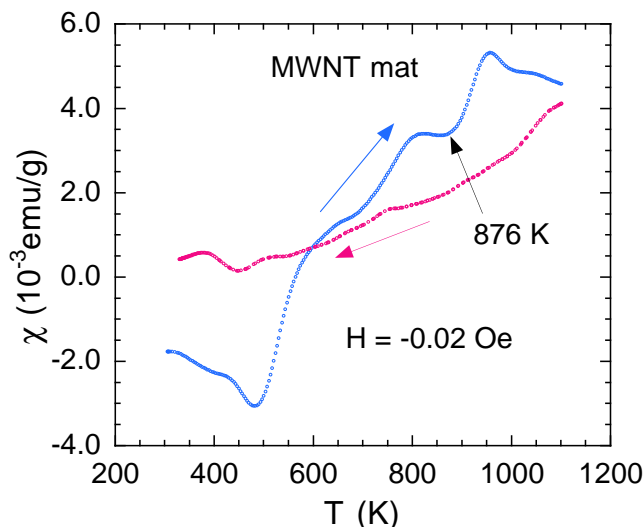


FIG. 1: The temperature dependence of the initial warm-up and cool-down susceptibilities in a field of -0.02 Oe for a 12.3 mg MWNT mat sample. The initial warm-up susceptibility at 482 K has a large negative value (about -3.05×10^{-3} emu/g), corresponding to about 8.4% of the full Meissner effect ($-1/4\pi$).

From the warm-up data, we clearly see a negative peak at about 482 K where the diamagnetic susceptibility is -3.05×10^{-3} emu/g, corresponding to about 8.4% of $-1/4\pi$ given that the specific weight of MWNTs is about 2.17 g/cm³. Such a strong diamagnetism cannot be explained by the orbital diamagnetism of MWNTs. This is because the magnitude of the total diamagnetic susceptibility at room temperature is 2.6×10^{-6} emu/g

in mechanically ground MWNTs [10, 11], which should be the upper limit of the magnitude of the orbital diamagnetic susceptibility. It is clear that the orbital diamagnetic susceptibility of MWNTs is over *three orders of magnitude* smaller than the observed diamagnetic susceptibility at 482 K. Moreover, the orbital diamagnetic susceptibility is predicted to be field independent [12], in contrast to a very strong field dependence of the diamagnetic susceptibility (see below).

It is known that a negative susceptibility peak can occur in granular superconductors for the warm-up measurement due to flux relaxation [13]. If the MWNT mat sample is a granular superconductor with an intergrain Josephson coupling temperature (T_{cJ}) above room temperature, some flux lines can be trapped in the regions of Josephson weak links at 300 K when the field is reduced from -0.5 Oe to -0.02 Oe. As the sample is warmed, the trapped flux lines will relax and move out of the sample, leading to a negative susceptibility peak slightly below T_{cJ} where the flux pinning force is greatly reduced due to the weakening of Josephson coupling [13]. If this interpretation is relevant, T_{cJ} of this MWNT mat sample is at least 482 K.

It is also interesting that there is a pronounced shoulder feature between 800 K and 900 K, which should arise from the ferrimagnetic ordering of γ -Fe₂O₃ impurities whose Curie temperatures are between 863-950 K (Ref. [14]). If we subtract the ferrimagnetic component of the susceptibility, the magnitude of the intrinsic diamagnetic susceptibility at 482 K will be much larger than 3.05×10^{-3} emu/g. Moreover, this cool-down susceptibility in -0.02 Oe for this CVD prepared sample is nearly the same as that in $+0.03$ Oe for an arc-discharge prepared sample [9] although the two samples have very different masses (12.3 mg versus 41 mg) and magnetic contaminations (5500 ppm versus 100 ppm), and are respectively subject to negative and positive fields (-0.02 Oe versus $+0.03$ Oe). Such consistency rules out explanations based on instrument artifacts and magnetic contaminations.

Figure 2a shows susceptibility versus temperature for our MWNT mat in a field of -0.02 Oe through thermal cycling. It is evident that the susceptibility becomes more diamagnetic upon thermal cycling. This is consistent with the fact that the trapped flux lines are progressively released upon heating up to 1100 K where the flux pinning force is much weaker. Similar behavior was observed [13] in polycrystalline Nb₃Sn, as shown in Fig. 2b.

Figure 3 shows both zero-field (ZFC) and field-cooled (FC) susceptibilities in a field of 2.1 Oe. It is apparent that the ZFC and FC susceptibilities show a significant difference throughout the whole temperature region. Moreover, when compared with the susceptibility in the field of -0.02 Oe, the diamagnetism in the field of 2.1 Oe disappears and the paramagnetic susceptibility at 1100 K is reduced by a factor of over 20. Although the tem-

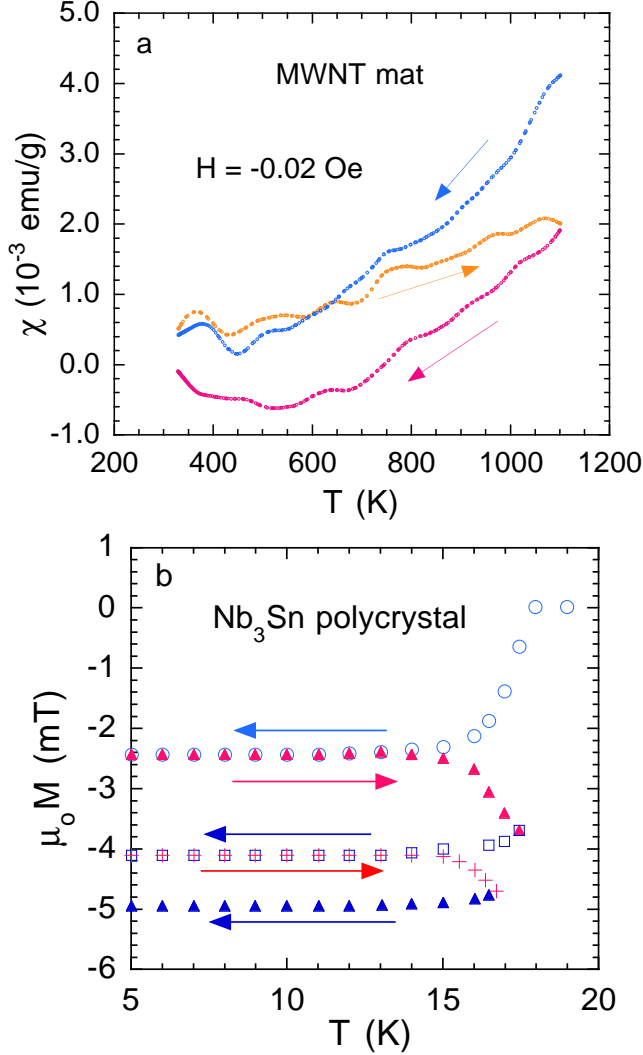


FIG. 2: (a) The susceptibility versus temperature in a field of -0.02 Oe through thermal cycling for the MWNT mat sample. (b) The magnetization versus temperature in a field of 100 Oe through thermal cycling for a polycrystalline Nb_3Sn . The data are reproduced from [13].

perature dependence of the FC susceptibility in such a low field has not been seen in any known ferromagnets or ferrimagnets, the result in Fig. 3 alone would also be consistent with a magnetic transition above 1100 K.

The very large paramagnetic susceptibility (about 4.6×10^{-3} emu/g) at 1100 K for the MWNT mat sample in the ultra-low field (see Fig. 1) cannot arise from magnetic contaminants. If this were caused by magnetic contaminants with the Curie temperatures higher than 1100 K, the candidates would only be Co and its alloys. For materials contaminated with magnetic impurities having very large intrinsic susceptibilities, the initial low-field susceptibility is independent of the intrinsic susceptibility and depends only on the shape (demagnetization factor) and concentration of the contaminant

[15]. The shape effect is averaged out through a random orientation so that the average demagnetization factor N should be about $1/3$ and the low-field susceptibility should be $1/(4\pi N) = 0.24$ emu/cm³. Given that the Co specific weight is 8.9 g/cm³, the low-field susceptibility of pure Co particles is calculated to be 0.027 emu/g. The precise elemental analysis on the non-carbon residual of the MWNT sample indicates that the Co concentration is below 3 ppm. The initial low-field susceptibility for this ultra-low Co concentration is therefore estimated to be $3 \times 10^{-6} \times 0.027$ emu/g = 8.1×10^{-8} emu/g, which is about *five orders of magnitude* smaller than the measured value.

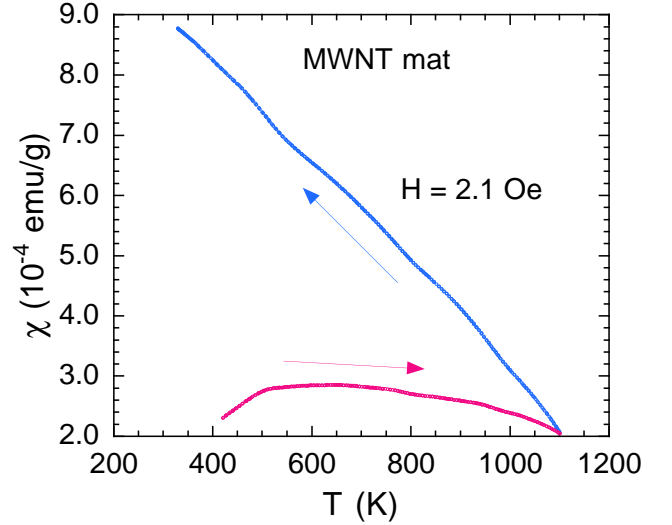


FIG. 3: The zero-field (ZFC) and field-cooled (FC) susceptibilities in a field of 2.1 Oe for the MWNT mat sample.

However, one might argue that the very large paramagnetic susceptibility at 1100 K in the ultra-low field might originate from a ferromagnetic/ferrimagnetic transition above 1100 K in an unknown carbon phase. Such a high Curie temperature in a carbon-related material, which does not have d electrons, would be very remarkable. Magnetic properties of amorphous-like carbon are found to depend on the hydrogen concentration [16]. For a hydrogen-rich phase, the Curie temperature is about 500 K and the saturation magnetization is about 10 emu/g (Ref. [16]). Polymerized fullerenes [17] and proton-irradiated graphite [18] also show ferromagnetic/ferrimagnetic transitions above room temperature. Thus, it is not impossible that the very large paramagnetic susceptibility at 1100 K arises from a ferromagnetic/ferrimagnetic ordering above 1100 K in an unknown carbon phase. However, the very rapid drop in the paramagnetic susceptibility with increasing field (e.g., 4.6×10^{-3} emu/g in -0.02 Oe and 2×10^{-4} emu/g in 2.1 Oe) in such a low field region (≤ 2.1 Oe) is difficult to explain in terms of *any* known ferromagnetic/ferrimagnetic transition. For normal ferromagnets/ferrimagnets, the initial low-field susceptibility *increases* with increasing

field in the field range less than 2.5 Oe [15, 19]. Even in the weak ferromagnet $\text{RuSr}_2\text{GdCu}_2\text{O}_8$, the susceptibility in the whole temperature region below the Curie temperature *increases* with increasing field for $H < 2.5$ Oe [20]. It is even more difficult to explain the large diamagnetic susceptibility and the negative susceptibility peak feature at about 482 K in terms of ferromagnetism/ferrimagnetism. Therefore, it appears unlikely that an unknown carbon phase with a ferromagnetic/ferrimagnetic transition above 1100 K is responsible for such unusual magnetic properties unless the ferromagnetic/ferrimagnetic phase would be very different from the conventional one.

Alternatively, the very large paramagnetic susceptibility at 1100 K and very large diamagnetic susceptibility at 482 K are consistent with the magnetic response in a granular superconductor [21] with $T_{c0} > 1100$ K. According to a theoretical simulation [21], the paramagnetic peak position occurs at about $0.9T_{c0}$, and the magnitude of the peak susceptibility decreases rapidly with increasing field in the ultra-low field region. Our data are consistent with this theoretical prediction, but inconsistent with any known ferrimagnetic/ferromagnetic transition. From Fig. 1, we also see that below the peak temperature, the susceptibility decreases with decreasing temperature and becomes negative at lower temperatures. This is also in agreement with the theoretical simulation for granular superconductors [21]. The large diamagnetic susceptibility at lower temperatures indicates that the diamagnetic Meissner effect outweighs the paramagnetic Meissner effect. The absence of diamagnetism in the field of 2.1 Oe is consistent with the fact that 2.1 Oe is much larger than the average intergrain lower critical field H_{c1} , which might be much lower than 0.02 Oe at 300 K. In this case, the diamagnetic Meissner effect is overwhelmed by the paramagnetic Meissner effect. In the high field range (>20 kOe), intergrain diamagnetic and paramagnetic Meissner effects will almost vanish so that the intragrain diamagnetic response dominates at low temperatures. The intragrain diamagnetic susceptibility is small because the magnetic penetration depth is much larger than the grain sizes [4, 8].

In summary, we have observed very unusual magnetic properties in MWNT mat samples. The data are inconsistent with any known physical phenomena except for granular superconductivity with an ultra-high intragrain transition temperature (> 1100 K). The much higher T_{c0} in the mat sample than that (~ 260 K) in the individual MWNT [4, 7, 8] may be due to more effective screening of the long-range Coulomb interaction, much less disorder, and more optimal doping in the mat samples. Alternatively, the very unusual magnetic properties observed in the MWNT mat samples might suggest the existence of

an unknown new physical phenomenon, which has similar magnetic properties as granular superconductors.

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